ORIGINAL PAPER

Fluorescence Characteristics of Bisphenol A in Room Temperature Ionic Liquids

**Huili Wang · Yujie Zou · Changli Li · Wenwei Wang ·
Minghua Zhang · Randy A. Dahlgren · Xuedong Wang**

Abstract Room temperature ionic liquids (RTILs) are emerging as a new class of 'green' solvents for use in a wide range of chemical processes. RTILs can sensitize or quench fluorescence of organic chemicals and their interactions still remain unclear, especially for weakly fluorescent chemicals. Herein, we report the effects of six RTILs on the fluorescence behavior of bisphenol A (BPA). The fluorescence intensities (FIs) of BPA in a RTIL-acetonitrile system were significantly quenched compared to acetonitrile. The quenching effect was stronger for $[C_nMIM]BF_4$ than $[C_nMIM]PF_6$. A decreasing trend of fluorescence lifetime (FL) of BPA was observed for $[C_6MIM]PF_6$ (4.26 to 3.86 ns) and $[C_{14}MIM]PF_6$ (4.15 to 3.78 ns) with increasing RTIL concentrations in the range of 1–10 mM. The quenching mode was consistent with a static quenching mechanism based on the consistency of FL and FI results. The emission bands of BPA and RTILs did not interfere with each other when RTILs were used as the solvent. The investigated RTILs enhanced the FIs of strongly fluorescing chemicals (12.0~19.0-fold for norfloxacin and 6.1~8.5-fold for dansyl chloride), but quenched those of weakly fluorescing chemicals (BPA). These results demonstrate that RTILs have different fluorescent effects on organic chemicals with different fluorophores. The interactions between RTILs and BPA result from many factors in addition to viscosity, such as solvent electrostatic dielectric constant, refractive index, density, polarization and molecular interaction. These results provide a theoretical foundation for application of RTILs in the analysis of weakly fluorescing chemical.

H. Wang · Y. Zou · C. Li · W. Wang (✉) · X. Wang (✉)
Department of Environmental Sciences, Wenzhou Medical
College, University-Town, Wenzhou, Zhejiang, China 325035
e-mail: wangwenwei@wzmc.edu.cn
e-mail: zjuwxd@163.com

M. Zhang · R. A. Dahlgren
Department of Land, Air and Water Resources,
University of California, Davis, CA 95616, USA

Introduction

Room temperature ionic liquids (RTILs) are emerging as an attractive new class of 'green' solvents to replace traditional solvents that often pose detrimental health and environmental effects. RTILs are composed of organic cations (e.g., imidazolium, pyrrolidinium, phosphonium, ammonium) and inorganic anions (Cl^-, PF_6^-, BF_4^-) or organic anions (trifluoromethysulfonate, $[CF_3SO_3]^-$; trifluoroethanoate, $[CF_3CO_2]^-$; etc.) [1]. They are widely used in the analytical chemistry field due to their unique properties, such as negligible vapor pressure, low melting point, high chemical and thermal stability, low moisture sensitivity, non-flammability, high electrical conductivity, and ability to dissolve in both hydrophilic and hydrophobic solutes [2–4]. RTILs are used in a wide range of chemical processes including extraction technology, chemical reaction, organic synthesis, electrochemistry, gas and liquid chromatography, mass spectrometry, and spectroscopy [5–12]. Among these applications, the use of RTILs in spectroscopy is worth special mention as RTILs are reported to both sensitize and quench fluorescence of chemicals with different fluorophores [13, 14]. For example, Wu and coworkers [15] found that the ionic liquids, $[C_4MIM]BF_4$, $[C_4MIM]NO_3$, $[C_6MIM]Br$, $[C_4MIM]PF_6$, $[C_6MIM]PF_6$ and $[C_8MIM]PF_6$, significantly enhanced the fluorescence intensities (FIs) of four isoquinoline alkaloids. Our previous investigation demonstrated that $[BMIM]PF_6$ quenched the fluorescence of 17 β-estradiol, but enhanced the fluorescence sensitivity of its derivatives with dansyl chloride (DNSCl) [16]. The FIs of norfloxacin were decreased with increasing alkyl chain length on the imidazolium ring of RTILs, and the main interaction between the ionic liquid
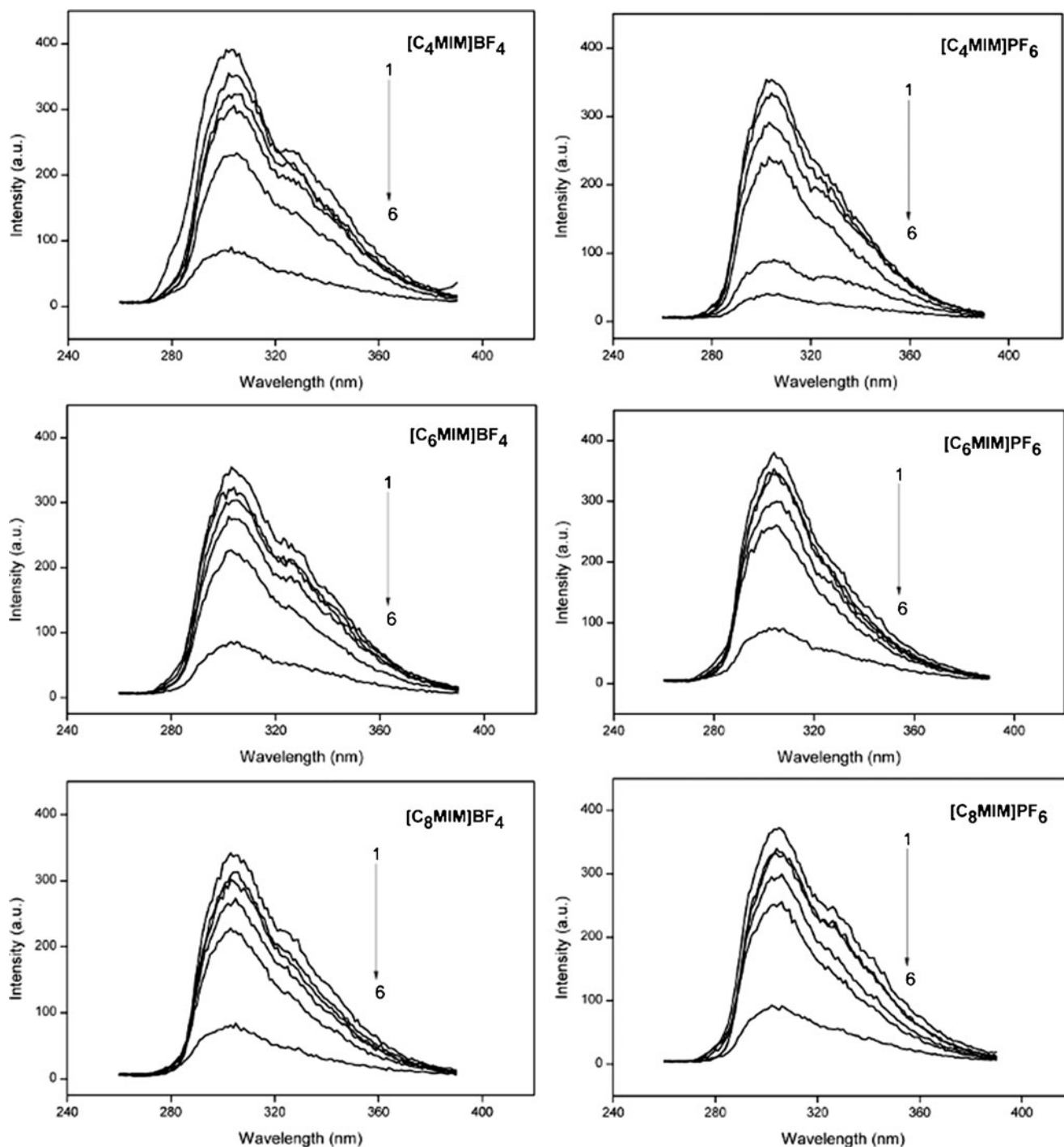
Fig. 1 The fluorescence emission spectra of BPA in acetonitrile and RTIL-acetonitrile systems. Note: *1–6* indicates 0, 0.05, 0.1, 0.5, 1.0, 5.0 mM RTILs

[C$_n$mim]Br and norfloxacin was shown not to consist of hydrogen bonding [17]. These past studies indicate that RTILs can have varying effects on chemicals with the different fluorophores. However, there is a paucity of data examining interactions between RTILs and weakly fluorescent chemicals, which hinders the efficient utilization of these 'green' solvents.

Bisphenol A (BPA) is an endocrine disrupting chemical that is widely used as a stabilizer in synthesis of polycarbonate and epoxy resins, unsaturated polyester-styrene resin and flame-retardant [18]. In recent years, BPA was shown to cause detrimental reproductive effects on wildlife and humans through altering endocrine function and may disrupt growth and development by interfering with the production, release,
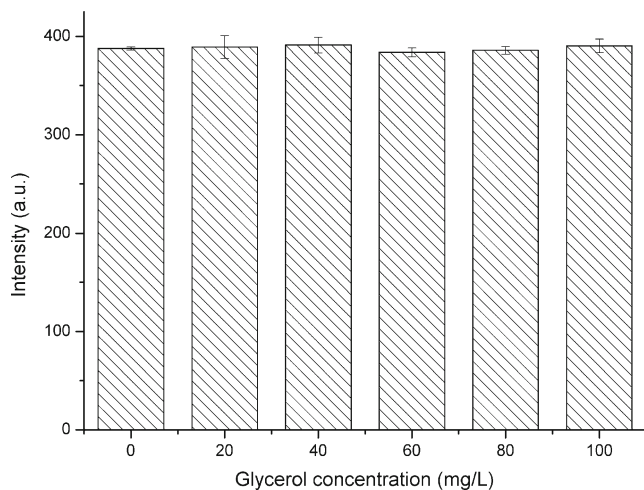
Fig. 2 The effect of solvent viscosity on the FIs of BPA

Fig. 4 Fluorescence emission spectra of BPA in [C_nMIM]BF$_4$ ($n=4$–16)

transport, metabolism, binding, and regulation of developmental processes [19]. The primary pathway of BPA introduction into the environment is from plastic-producing industry and landfill sites, which then enters into surface water and sediment through the sewage system [20].

Fluorescence determination is a quick and sensitive technique for analysis of organic chemicals with strong fluorophores. However, BPA is a weakly fluorescent chemical in aqueous solution due to its low quantum yield, and thus direct fluorescence determination is seldom applied at its trace analysis [21]. Studies examining interactions between RTILs and BPA can provide a theoretical foundation for application in the analysis of weakly fluorescent chemicals. In this study, 12 RTILs were chosen as representative solvents to analyze their effects on fluorescence spectra and fluorescence intensity of BPA. The effects of RTILs on strongly fluorescence chemicals (norfloxacin and DNSCl) and weakly fluorescence chemicals (BPA) were compared and analyzed.
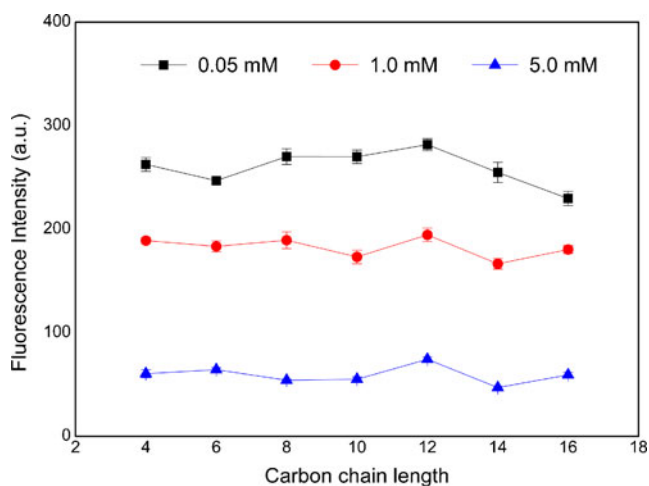

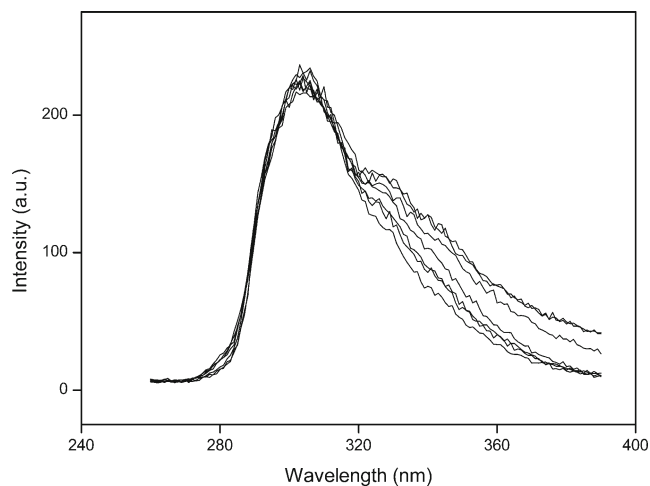Fig. 3 The effect of [C_nMIM]BF$_4$ ($n=4$–16) on the FI of BPA

Experimental

Materials

BPA was purchased from Sigma-Aldrich (St. Louis, MO, USA). All RTILs had stated purities of 99.0 % (Shanghai Chengjie Chemical Co., Shanghai, China) and were used as received. HPLC-grade acetonitrile was purchased from Jinshan Reagent Corporation (Wenzhou, China). Ultra-pure water was prepared with a Millipore Milli-Q plus system (Bedford, MA, USA).

Instruments

All fluorescent intensity analyses were performed on a model RF-5301PC spectrofluorometer (Shimadzu Corporation, Tokyo, Japan) coupled with a 150 W xenon arc lamp as the excitation source and single-grating monochromators as wavelength selection devices. The slit width was 5 nm. The excitation and emission wavelengths for BPA were 230 nm and 304 nm, respectively. All fluorescence spectra were corrected for the solvent blank. An Edinburgh FLS920 was used to measure fluorescence lifetimes using a nanosecond flashlamp as the excitation source. A single exponential fit was found adequate for the BPA-RTIL complexes, giving a chi-square of near unity (0.998–1.004).

Methods

A stock solution (10 mg/L) of BPA was prepared in acetonitrile and stored at 4 °C. Working solutions were obtained by appropriate dilution of the stock solution with ionic liquids or acetonitrile. To investigate the interaction between ionic liquids and BPA, the final concentrations of all RTILs were 0, 0.05, 0.1, 0.5, 1.0 and 5.0 mM. The tested BPA concentration was 0.1 mg/L unless otherwise stated. The test solution (2 mL)

Table 1 The FIs of BPA in [C_6MIM]BF_4, [C_8MIM]BF_4, [C_6MIM]PF_6 and [C_8MIM]PF_6

Concentrations of RTILs (mM)	[C_6MIM]BF_4	[C_6MIM]PF_6	[C_8MIM]BF_4	[C_8MIM]PF_6
0.05	247.0±2.6	274.9±4.0	270.1±7.6	279.5±0.7
0.1	228.0±5.4	255.4±7.1	265.4±6.3	266.8±8.5
0.5	189.7±6.5	235.9±9.8	195.7±3.7	227.7±11.3
1.0	183.4±5.4	196.8±7.8	189.4±8.2	203.3±4.1
5.0	64.4±1.8	66.3±2.0	54.1±1.0	66.0±2.7

Each treatment was in triplicate

was added to 1 cm² quartz cuvettes for fluorescence determination at 25 °C.

Results and Discussion

Fluorescence Properties of BPA in Acetonitrile and RTIL-acetonitrile Systems

Fluorescence emission spectra of BPA in acetonitrile and RTIL-acetonitrile systems are shown in Fig. 1. With addition of RTILs, such as [C_4MIM]BF_4, [C_6MIM]BF_4, [C_8MIM]BF_4, [C_4MIM]PF_6, [C_6MIM]PF_6 and [C_8MIM]PF_6, the fluorescence intensities (FIs) of BPA in the RTIL-acetonitrile system were significantly quenched compared to those in acetonitrile alone. In the quenching process, no obvious hypsochromic or bathochromic phenomenon of the emission maxima was observed. The presence of the non-bonding lone pair electrons, originating from electron-donating groups (-OH) in the benzene ring of BPA, leads to the fluorescence spectra of BPA more susceptible to polarity changes of solvent microenvironment. The excited state molecules of fluorescence chemicals can form complex with solvent molecules by hydrogen bond, which leads to the decreasing of FIs [22].

Effects of the Viscosities on Fluorescence Behavior of BPA

A series of different glycerol concentrations (0, 20, 40, 60, 80 and 100 mg/L) were prepared to investigate the effects of viscosities on the FIs of BPA. As shown in Fig. 2, the FIs of BPA were about 390 a.u. in the concentration range of 0–100 mg/L, and no significant differences of FIs were observed for the different glycerol concentration treatments. The results suggested that the solvent viscosity was independent of the FIs of BPA in this study.

Effects of the Different RTIL Concentrations on Fluorescence Behavior of BPA

At ambient conditions, the viscosity of most ionic liquids is in the range of 10~1,000 mPa.s, which is much more viscous than organic solvents, such as methanol and acetonitrile [23].
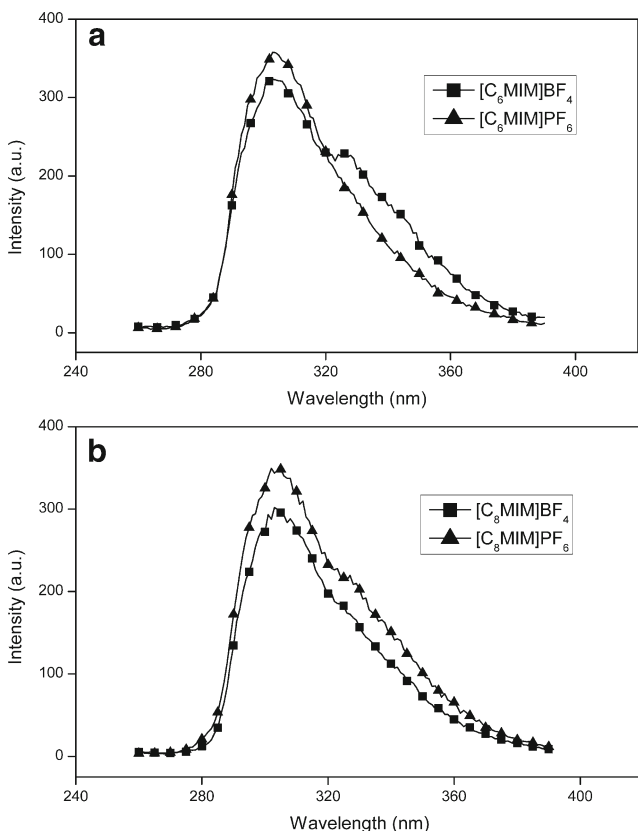

Fig. 5 Fluorescence emission spectra of BPA in [C_6MIM]BF_4, [C_8MIM]BF_4, [C_6MIM]PF_6 and [C_8MIM]PF_6
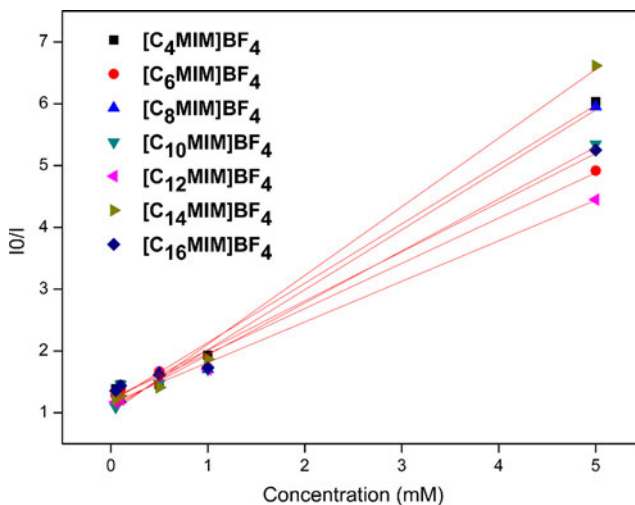

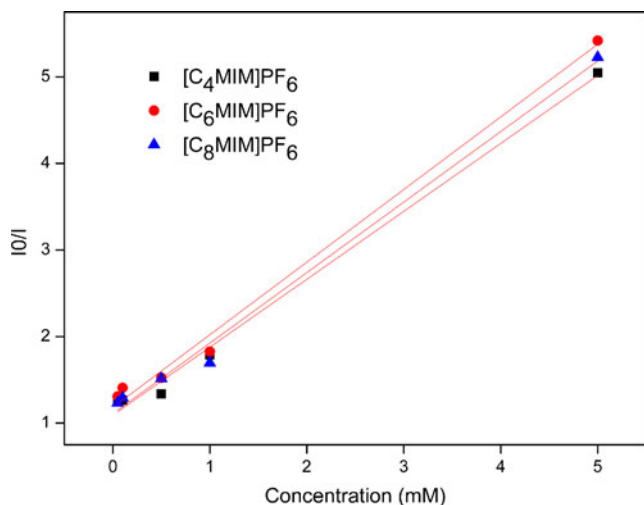**Fig. 6** The Stern-Volmer plot for BPA in [C_nMIM]BF_4

Fig. 7 The Stern-Volmer plot for BPA in [C_nMIM]PF_6

For example, the viscosity of [C_4MIM]PF_6 and [C_4MIM]BF_4 was reported to be 430 and 154 mPa.s, respectively, as compared to methanol with a viscosity of 0.58 mPa.s [24]. As for the same type of ionic liquid, the viscosity increases with increasing substituent atomic numbers [25]. The different concentrations of RTILs in solvents can result in a complex interplay with BPA due to their different physicochemical properties (e.g., viscosity, static dielectric constant, refractive index, density and polarizability). In this experiment, a series of RTIL concentrations ranging from 0.05 to 5.0 mM were prepared in acetonitrile to study their effects on the FI of BPA. As shown in Fig. 1, the FIs of BPA were decreased from about 350~400 a.u. in pure acetonitrile to 50~80 a.u. in 5.0 mM RTILs dissolved in acetonitrile. Therefore, RTILs had significant quenching effects on the fluorescence of BPA.

Effect of RTIL Cation

It has been reported that an increase of alkyl chain length on the imidazolium ring can lead to lower polarity [26] and higher of viscosity [4] when RTILs possess the same anion. Additionally, the FIs of organic chemicals will increase in a more viscous microenvironment [4]. The effects of different cations of

Table 2 The Stern-Volmer equation for BPA in [C_nMIM]BF_4

RTILs	Stern-Volmer equation	R^2	$K_{sv}/(\times 10^4$ L·mol$^{-1})$
[C_4MIM]BF_4	y=0.960x+1.175	0.991	0.960
[C_6MIM]BF_4	y=0.732x+1.224	0.993	0.732
[C_8MIM]BF_4	y=0.970x+1.051	0.992	0.970
[C_{10}MIM]BF_4	y=0.840x+1.097	0.989	0.840
[C_{12}MIM]BF_4	y=0.657x+1.157	0.996	0.657
[C_{14}MIM]BF_4	y=1.112x+0.999	0.994	1.112
[C_{16}MIM]BF_4	y=0.796x+1.219	0.990	0.796

Table 3 The Stern-Volmer equation for BPA in [C_nMIM]PF_6

RTILs	Stern-Volmer equation	R^2	$K_{sv}/(\times 10^4$ L·mol$^{-1})$
[C_4MIM]PF_6	y=0.785x+1.093	0.995	0.785
[C_6MIM]PF_6	y=0.839x+1.181	0.994	0.839
[C_8MIM]PF_6	y=0.815x+1.108	0.994	0.815

[C_nMIM]BF_4 (n=4, 6, 8, 10, 12, 14, 16) on the FIs of BPA were analyzed experimentally. According to the above-mentioned theory, the FIs of BPA should theoretically follow the order: [C_4MIM]$^+$ < [C_6MIM]$^+$ < [C_8MIM]$^+$ < [C_{10}MIM]$^+$ < [C_{12}MIM]$^+$ < [C_{14}MIM]$^+$ < [C_{16}MIM]$^+$. However, no consistent trend or obvious differences for the FIs of BPA were observed with the increase in carbon chain length on the imidazolium ring (Fig. 3). The fluorescence emission spectra of BPA remained nearly constant, suggesting no significant effect of RTIL cations on the fluorescence behavior of BPA (Fig. 4).

Effect of RTIL Anion

The FIs of BPA with respect to RTILs with different anions are listed in Table 1. With the addition of RTILs, a significant quenching effect on the FI of BPA was observed in the concentration range of 0.05–5.0 mM. In addition, the quenching effect was stronger for [C_nMIM]BF_4 than [C_nMIM]PF_6. Meanwhile, the fluorescence emission spectra of BPA remained nearly constant, showing a similar phenomenon to the differential cation effect (Fig. 5). Huddleston et al. [27] found that the viscosity of imidazolium RTILs with different anions follows the order: BF_4^- < PF_6^-. Generally, the greater the symmetry of the anion, the higher the viscosity of RTILs [28]. The high viscosity may inhibit molecular diffusion and collision of excited-state BPA molecules. Thus, the quenching effect was stronger for [C_nMIM]BF_4 than [C_nMIM]PF_6.

Fluorescence Quenching Mechanism

The FIs of BPA significantly decreased in the RTIL microenvironment because of molecular interaction, and thus RTILs

Table 4 The FLs of BPA at different concentrations

BPA (mg/L) in acetonitrile	λ_{ex}/nm	λ_{em}/nm	τ/ns	$\chi2$
0.05	230	304	4.182±0.007	1.004
0.1	230	305	4.276±0.012[**]	1.002
0.3	230	304	4.283±0.016[**]	0.999

(1) Each treatment was in triplicate

(2) "[**]" indicates the significant level at $p<0.01$ compared with 0.05 mg/L BPA treatment

can act as a fluorescence-quencher. Fluorescence quenching can result from static and dynamic quenching mechanisms. Static quenching refers to formation of a ground state fluorophore–quencher complex that does not emit a photon. In contrast, dynamic quenching refers to formation of an excited state fluorophore-quencher complex [28]. Fluorescence quenching is generally described by the Stern-Volmer equation:

$$F_0/F = 1 + K_q\tau_0[Q] = 1 + K_{sv}[Q]$$

where F_0 and F are the fluorescence intensities of the fluorophore in the absence and presence of quenchers, respectively; K_{sv} and K_q are the Stern–Volmer and the bimolecular quenching constants, respectively; and τ_0 is the lifetime of the fluorophore in the absence of a quencher. Plots of F_0/F versus concentrations of RTILs are shown in Figs. 6 and 7. The fair-to-good linear correlation coefficient (R^2) and the quenching constant (K_{sv}) are shown in Tables 2 and 3. As reported by Geng et al. [29], the Stern-Volmer quenching constant for dynamic quenching was less than 1.0×10^3 L/mol. Therefore, the low Stern-Volmer constants determined for fluorescence quenching of BPA by 10 RTILs in this study infers a static quenching mechanism. In addition, the quenching efficiency showed an irregular trend.

Effects of RTILs on the FLs of BPA

The fluorescence lifetimes (FLs) of BPA ranged from 4.18 to 4.28 ns in the investigated concentration range of 0.05–0.3 mg/L (Table 4). No significant differences for FL were observed among the different BPA concentrations, especially for 0.1 and 0.3 mg/L treatments (FLs 4.27 and 4.28 ns). Therefore, the test concentration of BPA was set at 0.1 mg/L to investigate the effects of RTILs on FLs. As for the two RTILs, a decreasing trend of FL was observed for [C6MIM]PF6 (4.26 to 3.86 ns) and [C14MIM]PF6 (4.15 to 3.78 ns) with increasing RTIL concentrations in the 1–10 mM range (Table 5). Additionally, the longer carbon chain length on the imidazolium ring could lead to shorter FL for the same RTIL concentrations. The FL profiles are shown in Fig. 8a for [C6MIM]PF6 and 8b for [C14MIM]PF6. A consistent trend was observed between FI and FL for BPA in RTILs, i.e., the decreasing FL was consistent with the quenching effect on FL for BPA.

The ratio of τ_0 (FL for control) to τ_1 (FL for treatment) can also be applied for judging the quenching mechanism. If τ_0/τ_1 is close to 1, the quenching mode is a static quenching mechanism, and if it is close to F_0/F, the quenching mode is considered a dynamic quenching mechanism. It can be estimated from Table 5 that τ_0/τ_1 ranges from 1.0018 to 1.1306 with values very close to 1. However, in the RTIL concentration

Table 5 The FLs of BPA in two RTILs

BPA+[CnMIM]PF6	C/mM	λ_{ex}/nm	λ_{em}/nm	τ/ns	$\chi2$
BPA (0.1 mg/L)	0	230	304	4.276±0.012	1.002
BPA+[C6MIM]PF6	1	230	304	4.268±0.008	1.001
	5	230	304	4.034±0.012[**]	0.998
	10	230	304	3.863±0.016[**]	0.998
BPA+[C14MIM]PF6	1	230	304	4.155±0.020[**]	0.999
	5	230	304	3.907±0.025[**]	1.002
	10	230	304	3.782±0.009[**]	1.000

"**" indicates the significant level at $p<0.01$ compared with 0 mM RTILs treatment

range of 1 to 10 mM, F_0/F of BPA varied between 1.63 and 4.58, thus showing an inconsistent trend with τ_0/τ_1. Therefore, the quenching mode is considered a static quenching mechanism based on the consistency of interpretations from FL and FI data.

Effect of RTIL Optical Property

A number of photophysical studies examining RTILs indicated that all imidazolium ionic liquids exhibited an excitation wavelength-dependent fluorescence behavior [6, 29, 30]. In this study, the emission behavior of RTILs was
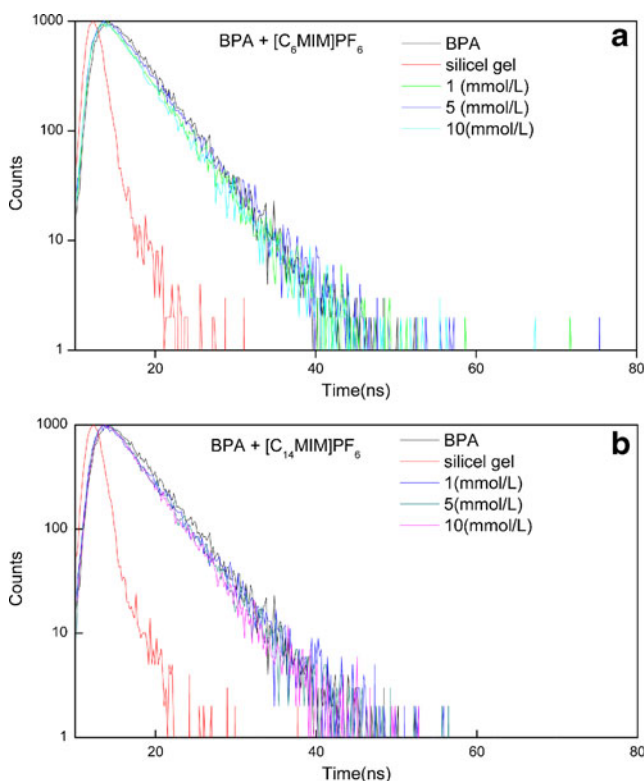

Fig. 8 The fluorescence lifetimes of BPA at different RTIL concentrations

observed at a short excitation wavelength of 276 nm. Figure 9 shows emission spectra of 0.4 % RTILs in acetonitrile [17]. The general emission characteristics of the investigated imidazolium ionic liquids are quite similar [6, 30]. The emission band of all imidazolium ionic liquids was observed around 400 to 420 nm. For short excitation wavelengths, this band does not shift in response to variations in the excitation wavelength [6]. Meanwhile, the maximum emission band of BPA was observed near 304 nm, suggesting that the emission band of BPA and RTILs did not appreciably interfere with each other. Additionally, the FI of BPA was much higher (>3-fold) than that of the RTILs. As a result, the optical properties of RTILs do not appreciably affect the fluorescent emission of BPA when used as the solvent.

The Different Effects of RTILs on Chemicals with Different Fluorophores

In this investigation, the six RTILs all showed significant quenching effects on BPA, a weakly fluorescing compound. In order to compare the different effects of RTILs on organic chemicals with different fluorophores, we studied the characteristics of strongly fluorescing chemicals in RTILs. Using the maximum emission wavelength of 412 nm, the FI of norfloxacin (NFLX) increased by 12.0~19.0-fold in $[C_nMIM]BF_4$/methanol and 1.5~17.0-fold in $[C_nMIM]PF_6$/methanol solutions (Fig. 10a) as compared to NFLX in methanol alone [17, 25]. In addition, RTILs had significant enhancement effects on the FIs of DNSCl compared to those in water. At 5 mg/L, $[C_4MIM]PF_6$, $[C_6MIM]PF_6$ and $[C_8MIM]PF_6$ increased the FI of DNSCl by 8.5, 7.6 and 6.1 times, respectively, compared to water. Similarly, at 50 mg/L, $[C_4MIM]PF_6$, $[C_6MIM]PF_6$ and $[C_8MIM]PF_6$, increased the FI of DNSCl by 7.9, 7.6 and 7.0 times, respectively, compared to that in
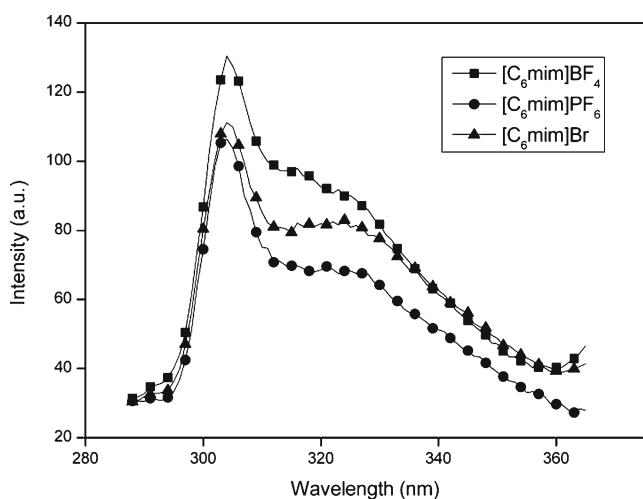
water alone (Fig. 10b). The fluorescence enhancement or quenching was dependent on the type and concentrations of fluorescent substances and characteristics of the RTILs. The increase in quantum yields of rhodamine B, pyronine B, and 1,10-phenanthroline in the presence of $[C_4MIM]PF_6$ demonstrated fluorescent enhancement by the ionic liquids. The most significant enhancement effects on fluorescing chemicals were observed in micelles of $[C_4MIM]PF_6$, with an obvious hypsochromic shift [8]. The previous results demonstrate that RTILs, such as $[C_4MIM]PF_6$, have a different effect on strongly versus weakly fluorescing compounds, namely an enhancing effect for strongly fluorescing chemicals (e.g., DNSCl, rhodamine B, 1,10-phenanthroline, NFLX), and a quenching effect for weakly fluorescing chemicals (e.g., 17α-estradiol (EE1), 17β-estradiol (E2) and BPA). The former phenomenon is in agreement with observations by Fletcher et al. [23] who found the emission from alternant PAHs was quenched while that from nonalternant PAHs was not [4]. However, further research is required to understand the exact mechanism responsible for these differences.
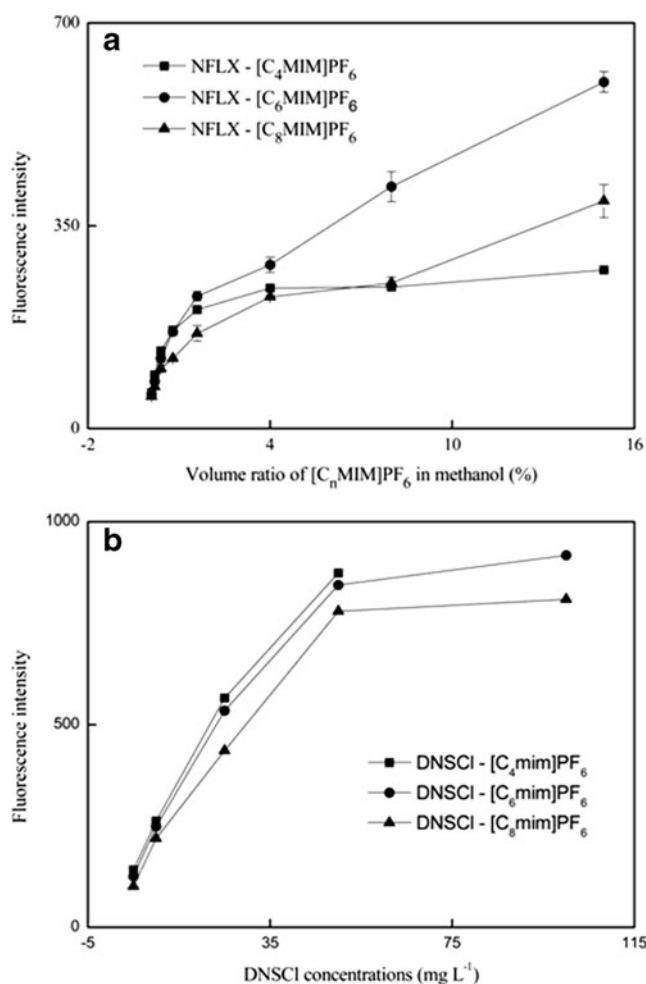

Fig. 10 The effects of $[C_nmim]PF_6$ on the FIs of NFLX and DNSCl

Fig. 9 Emission spectra of 0.4 % RTILs in methanol

Conclusions

In this study, we determined the effects of six RTILs on the fluorescence characteristics of BPA. The main conclusions are summarized as follows: (i) The FI of BPA decreased with increasing concentration of RTILs (0.01–5.0 mM); (ii) In the glycerol concentration range (0–100 mg/L), the solvent viscosity was independent of the FIs of BPA; (iii) The quenching efficiency of RTILs on BPA was $[C_nMIM]BF_4>[C_nMIM]PF_6$ and there was no obvious differences for the FIs of BPA with increasing carbon chain length on the imidazolium ring; (iv) The fluorescence quenching by the six RTILs was consistent with a static quenching mechanism based on the Stern-Volmer equation; The quenching mode is also considered a static quenching mechanism according to the consistency of interpretation from FL and FI data. Although FIs of fluorescence chemicals mainly depend on their structural properties, the environmental factors, especially for medium, may have a strong influence on their molecular fluorescence. Especially for the polar fluorophores in the aromatic ring, their fluorescence spectra are very susceptible to solvents, which include a "special solvent effect" indicating special chemical action between fluorophors and solvent molecules. In this research, solvent viscosity had no significant effect on the FIs of BPA, and also no obvious hypsochromic or bathochromic phenomenon of the emission maxima was observed. The quenching effect of BPA due to addition of RTILs was much smaller than that due to "encounter frequency" controlled by diffusion. In such cases, Ksv was independent of the solvent viscosity, which ruled out the possibility of dynamic quenching mechanism. However, the most appropriately distinguishing method between static and dynamic quenching is based on fluorescence lifetime. When the FLs remain nearly unchanged (i.e., $\tau_0/\tau_1 \approx 1$) in the presence of quencher, the quenching is referred to static quenching mechanism [21]. (v) The investigated RTILs had different fluorescent effects on organic chemicals with different fluorophores, namely, an enhancing effect for strongly fluorescing chemicals (e.g., DNSCl, NFLX) and a quenching effect for weakly fluorescing chemicals (e.g., BPA).

References

1. Sun P, Armstrong DW (2010) Ionic liquids in analytical chemistry. Anal Chim Acta 661:1–16

2. Vygodskii YS, Mel'nik OA, Lozinskaya EI, Shaplov AS, Malyshkina IA, Gavrilova ND, Lyssenko KA, Antipin MY, Golovanov DG, Korlyukov AA, Ignat'ev N (2007) The influence of ionic liquid's nature on free radical polymerization of vinyl monomers and ionic conductivity of the obtained polymeric materials. Polym Adv Technol 18:50–63

3. Mutelet F, Revelli AL, Jaubert JN, Sprunger LM, Acree WE Jr, And Baker GA (2010) Partition coefficients of organic compounds in new imidazolium and tetralkylammonium based ionic liquids using inverse gas chromatography. J Chem Eng Data 55:234–242

4. Wakai C, Oleinikova A, Ott M, Weingärtner H (2005) How polar are ionic liquids? Determination of the static dielectric constant of an imidazolium-based ionic liquid by microwave dielectric spectroscopy. J Phys Chem B 109:17028–17030

5. Vidal L, Riekkola ML, Canals A (2012) Ionic liquid-modified materials for solid-phase extraction and separation: a review. Anal Chim Acta 715:19–41

6. Guerra-Abreu L, Pino V, Anderson JL, Afonso AM (2008) Coupling the extraction efficiency of imidazolium-based ionic liquid aggregates with solid-phase microextraction-gas chromatography–mass spectrometry: application to polycyclic aromatic hydrocarbons in a certified reference sediment. J Chromatogr A 1214:23–29

7. Tao Y, Liu FJ, Hu XL, Li HC, Wang T, Jiang GB (2009) Hollow fiber supported ionic liquid membrane microextraction for determination of sulfonamides in environmental water samples by high-performance liquid chromatography. J Chromatogr A 1216:6259–6266

8. Cruz-Vera M, Lucena R, Cardenas S (2009) One-step in-syringe ionic liquid-based dispersive liquid–liquid microextraction. J Chromatogr A 1216:6459–6465

9. Bian M, Zhang ZJ, Yin H (2012) Effects and mechanism characterization of ionic liquids as mobile phase additives for the separation of matrine-type alkaloids by liquid chromatography. J Phar Biomed Anal 58:163–167

10. Martín-Calero A, Pino V, Ayala JH, González V, Afonso AM (2009) Ionic liquids as mobile phase additives in high-performance liquid chromatography with electrochemical detection: application to the determination of heterocyclic aromatic amines in meat-based infant foods. Talanta 79:590–597

11. Breitbach ZS, Armstrong DW (2008) Characterization of phosphonium ionic liquids through a linear solvation energy relationship and their use as GLC stationary phases. Anal Bioanal Chem 390:1605–1617

12. Payagala T, Zhang Y, Wanigasekara E, Huang K, Breitbach ZS, Sharma PS, Sidisky LM, Armstrong DW (2009) Trigonal tricationic ionic liquids: a generation of gas chromatographic stationary phases. Anal Chem 81:160–173

13. Bose S, Wijeratne AB, Thite A, Kraus GA, Armstrong DW, Petrich JW (2009) Influence of chiral ioinic liquids on stereoselective fluorescence quenching by photoduced electron transfer in a naproxen dyad. J Phys Chem B 113:10825–10829

14. Devi VS, Maji S, Viswanatha KS (2011) Novel room temperature ionic liquid for fluorescence enhancement of Eu^{3+} and Tb^{3+}. J Lumin 131:739–748

15. Wu H, Zhang LB, Du LM (2011) Ionic liquid sensitized fluorescence determination of four isoquinoline alkaloids. Talanta 85:787–793

16. Wang XD, Li YY, Du XW, Lin ZK, Huang CJ (2011) Effects of room temperature ionic liquids on fluorescence characteristics of 17β-estradiol and its derivative. J Fluoresc 21:1643–1648

17. Zou YJ, Wang HL, Wang WW, Ma MP, Wang P, Wang CJ, Wang XD (2012) The effect of imidazolium room temperature ionic liquids on the fluorescent properties of Norfloxacin. Luminescence doi:10.1002/bio.1382

18. Wang X, Zeng HL, Zhao LX, Lin JM (2006) Selective determination of bisphenol A (BPA) in water by a reversible fluorescence

sensor using pyrene/dimethyl β-cyclodextrin complex. Anal Chem Acta 556:231–318

19. Vandenberg LN, Hauser R, Marcus M, Olea N, Welshons WV (2007) Human exposure to bisphenol A (BPA). Reprod Toxicol 24:139–177

20. Sajiki J, Yonekubo J (2004) Leaching of bisphenol A (BPA) from polycarbonate plastic to water containing amino acids and its degradation by radical oxygen species. Chemosphere 55:861–867

21. Braunrath R, Cichna M (2010) Sample preparation including sol-gel immunoaffinity chromatography for determination of bisphenol A in canned beverages, fruits and vegetables. J Chromatogr A 1062:189–198

22. Xu JG, Wang ZB (2006) Fluorimetry, 3rd edn. Science and Technology Press, China

23. Fletcher KA, Pandey S, Storey IK, Hendricks AE, Pandey S (2002) Selective fluorescence quenching of polycyclic aromatic hydrocarbons by nitromethane within room temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. Anal Chim Acta 453:89–95

24. Deng YQ (2006) Ionic liquid: property, synthesis and applications. China Petrochemical Press, Beijing

25. Hyun BR, Dzyuba SV, Bartsch RA, Quitevis EL (2002) Intermolecular dynamics of room-temperature ionic liquids: femtosecond optical kerr effect measurements on 1-alkyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imides. J Phys Chem A 106:757

26. Ho TD, Canestraro AJ, Anderson JL (2011) Ioniic liquids in solid-phase microextraction: a review. Anal Chim Acta 695:18–43

27. Huddleston JG, Visser AE, Reicher WM (2001) Characterzation and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. Green Chem 3:156–164

28. Geng F, Zheng L, Yu L, Li G, Tung C (2010) Interaction of bovine serum albumin and long-chain imidazolium ionic liquid measured by fluorescence spectra and surface tension. Process Biochem 45:306–311

29. Obliosca JM, Arco SD, Huang MH (2007) Synthesis and optical properties of 1-alkyl-3-methylimidazolium lauryl sulfate ionic liquids. J Fluoresc 17:613–618

30. Paul A, Mandal PK, Samanta A (2005) On the optical properties of the imidazolium ionic liquids. J Phys Chem B 109:9148–9153